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## PROTECTIVE TECHNOLOGICAL COATINGS FOR HEAT-TREATMENT OF VKS HIGH-STRENGTH STEELS

**S. S. Solntsev,[1] V. A. Rozenenkova,[1] N. A. Mironova,[1] and S. V. Gavrilov[1]**

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Universal fritless coatings for heat-treatment of VKS high-strength steels have been developed. The kinetics of oxidation of VKS steel with and without a coating has been investigated. It has been shown that it is effective to use a fritless coating on a half-done VKS steel part.

***Key words:*** fritless ceramic coatings, oxidizability, high-strength steels.

VKS high-strength steels are distinguished by intense oxidation during heating in an ordinary oxidative air medium. These steels must be protected from oxidation during thermomechanical working, hardening, annealing, normalizing, and homogenizing.

It is undesirable to use different grades of protective technological coatings (PTC) for each type of heat-treatment of steel, because the fabrication of coatings becomes more labor-intensive and the finished parts more expensive.

The study of regularities in the variation of the properties and structural particulars of heterogeneous multicomponent glass-ceramic and ceramic systems has made it possible to develop ÉVT-70 and -70M glass-ceramic slip coatings for annealing VKS steel after soaking at 900 – 950°C for 5 h and an ÉVT-77 ceramic, fritless, charge coating (soaking at 1150 – 1200°C, 1 h).

The problem of the present work was to develop a universal fritless ceramic PTC for the complete heat-treatment cycle for large-size blanks made of high-strength VKS steel. A fritless ceramic coating must be serviceable in a wide temperature range (780 – 1200°C) and provide reliable oxidation protection for steel during prolonged soaking (1200°C to 5 h).

Because there are no published sources of information on coatings for protecting VKS steels or theoretical data on the synthesis of such coatings, a series of studies aimed at solving this complex and topical scientific-technical problem was conducted in the present work.

The investigations aimed at the development of compositions for universal, ceramic, fritless, slip coatings and the technology for producing and using them and the study of their protective action were conducted in two stages.

At the first stage the PRC were developed by heating laboratory samples of VKS high-strength steel in the temperature range 780 – 1200°C with 1 – 3 h soaking and annealing for 1 h at 780°C.

The prospects for using the coatings were evaluated from the results of comparative heat-tolerance tests performed on coated and uncoated steel samples by means of thermogravimetric analysis (GOST 6130).

The resistance of the coatings to high temperatures during prolonged soakings was evaluated according to their phase stability, which was determined by the x-ray structural method using the computer programs Express, Outset, and Phan. A DRON-4 diffractometer with monochromatic $CuK_{\alpha}$ radiation was used to obtain the diffraction patterns of the samples.

The substrate materials on which the experimental coating compositions were deposited consisted of samples and fragments simulating chassis parts made of VKS high-strength steels.

The quality of the initial materials and coatings (main component content, presence of impurities, moisture content and particle size of the powders, and others) was evaluated by standard methods: moisture content of the powders — GOST 9758, conventional viscosity — on VZ-246 apparatus following GOST 8420, fineness (specific surface area) of the particles $S_{sp}$ — Analizette-22 apparatus, density — aerometer following GOST 18481, and pH — GOST 211193. An MB-10 binocular microscope was used to evaluate the quality of the metal surface. Coated samples were heat treated in high-temperature furnaces with automatic control systems.

[1] Federal State Unitary Enterprise All-Russia Institute of Aviation Materials (FGUP VIAM), Moscow, Russia.



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The oxidizability of the VKS steel samples was investigated as a function of time and temperature regimes during a full heat-treatment cycle. The effect of time, temperature, and the gas medium on the intensity of the oxidation of VKS steel was studied. To obtain comparative data the VKS steel samples were heated in air and inert argon media. The weight increase of the samples at each stage of heating and the total weight increase over a complete heat-treatment cycle were determined.

The studies established that temperature, time, and the gas medium are the main factors influencing the intensity of the oxidation of VKS steel. As the heating temperature increases from 780 to 1200°C the weight increase of the samples increases from 0.035 – 0.04 to 1.8 – 2.2 $kg/m^2$, increasing the heating time at 900°C from 1 to 3 h increases the weight of the samples from 0.04 to 1.0 $kg/m^2$. The weight increase of VKS steel during a complete cycle of heat treatment in air 2.5 – 2.8 $kg/m^2$ is 10 – 12 times greater than the weight increase of samples heat-treated in an inert gas (argon) medium — 0.18 – 0.22 $kg/m^2$.

Fritless protective coating compositions were prepared (using domestic raw material) on the basis of $Al_2O_3$ – RO ceramic, ceramic with the composition $2MgO \cdot Al_2O_3 \cdot 5SiO_2$ and $CaO \cdot 6Al_2O_3$, which additionally contained a synthetic modifier. The problem of finding fritless coatings for the working temperature interval 780 – 1200°C was complicated by the fact that such coatings must form a reliable protective layer not only at high but also relatively low temperatures. The temperature range of coating serviceability can be expanded by using fluxes such as boron anhydride and fine powders (for example, zinc and calcium oxides), which in negligible quantities lower the sintering temperature of ceramic based on aluminum and silicon oxides.

To accelerate sintering, increase the density of the protective layer of the coating, and stabilize the physical-chemical properties of coatings all initial components were subjected to prolonged comminution in porcelain drums on a roller mill. The effect of grinding time from 30 to 150 h on the specific surface area of the powders obtained was investigated. It was determined that increasing the grinding time from 30 to 150 h increases the fineness of the powders of the initial components: $CaCO_3$ — from 300 to 1250 $m^2/kg$; $MgCO_3$ — from 450 to 1400 $m^2/kg$; and, ZnO — from 600 to 1850 $m^2/kg$.

Experimental slips of ceramic PTC with different modifier contents were prepared by fritless technology and the influence of the coating composition on the coating formation regime was studied. The main requirement for forming PTC was maximizing the density of the protective coating impeding oxygen diffusion to the metal at $T \leq 950$°C over the shortest possible time. It was determined that increasing the mass content of boron anhydride in the composition of the fritless coating to 5%[2] decreases the coating formation temperature from 950 to 750°C, increasing the zinc oxide content to 5% lowers the coating formation temperature from 950 to 850°C, and in the process the density of the protective layer for all experimental compositions reaches the maximum density 3100 – 3200 $kg/m^3$ over soaking time 3 – 5 min, which secures reliable protection of the surface of steel parts at the early stages of heat treatment.

The effect of the composition of a fritless PTC on its protective efficiency was studied during a complete heat-treatment cycle for VKS high-strength steel. The effect of the modifier content (boron anhydride and zinc oxide) in a fritless ceramic coating in the system $Al_2O_3$ – RO on the oxidizability of VKS high-strength steel during a complete heat-treatment cycle was studied.

The effectiveness of the protective action of coatings was determined from the results of heat-tolerance (oxidizability) tests performed on VKS samples with experimental coatings. It was determined that introducing into a ceramic coating composition the modifier ZnO in amounts 3 – 5% decreases the oxidizability of VKS steel from 0.11 to 0.05 $kg/m^2$. Introducing 1% $B_2O_3$ into the coating composition lowers the oxidizability of steel only negligibly (0.085 $kg/m^2$). Increasing $B_2O_3$ content (to 5%) increases the oxidizability of steel.

Structural analysis of the materials in the initial state and after heating at 1200°C and soaking up to 3 h did not show any appreciable differences. The x-ray diffraction patterns of the samples are practically identical. After heat treatment at 1200°C for 3 h a negligible portion of the coating material transitions into an amorphous state. The data obtained from x-ray phase analysis shows that the experimental compositions of a ceramic fritless coating are highly stable.

The optimal composition of a fritless protective technological coating, labeled as ÉVT-77M, was determined from an analysis of the data on the effectiveness of the protective action of the coatings and from the results of x-ray phase analysis.

The PTC fabrication technology was determined. It includes the following production operations: quality control and preparation of the initial components, preparation of high-temperature ceramic sinter, preparation of the coating slip, and checking the quality of the coating slip.

The use of the ÉVT-77M coating during a complete heat-treatment cycle for VKS steel decreased the oxidizability of the steel 30-fold. The process of fabricating an ÉVT-77M coating is cost-effective because it employs fritless technology, which eliminates the labor-intensive process of obtaining frit.

The technology developed was used to fabricate an experimental batch of coating slip and to determine the technological properties: specific surface area of the particles — 1000 $m^2/kg$, viscosity — 19 sec, suspension density — 2400 $kg/m^3$, and pH — 6.2.

ÉVT-77M slip for PTC was deposited on VKS steel samples and the protective effectiveness of the coating was evaluated during a complete heat-treatment cycle for the high-strength steel was evaluated. The results were as follows: the

[2] Here and below, content by weight.

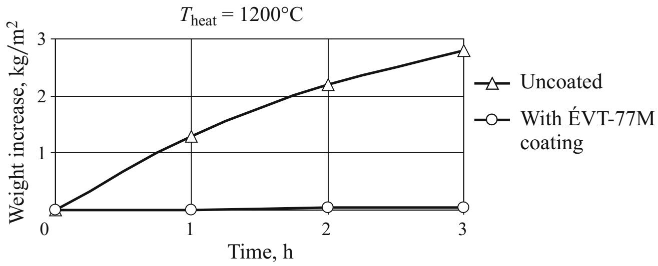


**Fig. 1.** Oxidation kinetics of VKS-180 steel during a complete heat-treatment cycle.

weight increase of coated and uncoated samples was 0.05 – 0.06 and 2.5 – 2.8 kg/m$^2$, respectively; the oxidized layer size with and without a coating was 0.14 – 10.5 and 2.8 – 2.9 mm, respectively. Figure 1 shows that change of the weight increase (oxidation) of the VKS high-strength steel samples with ÉVT-77M fritless ceramic with and without a coating.

It was determined that the ÉVT-77M coating affords reliable protection of VKS high-strength steel during a complete heat-treatment cycle and lowers the oxidizability of steel by a factor of 46 – 50.

The problem addressed at the second stage of this work was to improve the ÉVT-77M coating for use in the heat-treatment of large-size blanks of VKS steel with the heating time at 1200°C increased to 5 h.

Zirconium dioxide was chosen as the modifier for increasing the temperature stability of an ÉVT-77M coating. The drawback of $ZrO_2$-based ceramic is relatively low phase stability — to 1080°C. It is known that introducing magnesium oxide in amounts to 10% increases the phase stability of $ZrO_2$-based ceramic by raising the temperature of the transformation of the monoclinic modification of $ZrO_2$ into the tetragonal modification to 1500°C.

The experimental batches of slips for the ÉVT-77M ceramic coating with zirconium and zinc oxide additives were studied experimentally.

It was established that increasing the $ZrO_2$ content in the experimental slip batches to 10% increases the density of the suspension from 2400 to 2550 kg/m$^2$; other technological properties are similar to those of the slip for the ÉVT-77M coating. The protective effectiveness of the coatings was determined from the results of thermogravimetic tests and studies of the phase stability of PTC. Slips of the experiment coating compositions were deposited on VKS-180 steel fragments, simulating large-size parts of a chassis, by dipping (conventional slip viscosity 19 sec). The finished samples were dried in air for 24 h, after which their surface quality was evaluated visually for the absence of defects.

To evaluate the effect of the $ZrO_2$ content in fritless ceramic coating in the system $Al_2O_3$ – RO on the protective effectiveness of the coating during heat-treatment of VKS steel, a complete heat-treatment cycle in a furnace with an air atmosphere was conducted.

It was determined that increasing the $ZrO_2$ content in ÉVT-77M fritless coating with 3, 5, and 10% additions decreases the oxidizability of VKS steel samples during heat treatment by a factor of 1.8 – 2 compared an ÉVT-77M coating and a factor of 25 – 30 compared with the oxidizability of uncoated steel samples. Increasing the $ZrO_2$ content from 5 to10% has practically no effect on the oxidizability of coated steel samples. Subsequent studies were performed on a coating with 5% $ZrO_2$.

To determine the phase stability of the coatings, PTC samples were prepared with 5% $ZrO_2$ and heat-treated in the following regimes: No. 1 — 1200°C, 1 h; No. 2 — 1200°C, 3 h; No. 3 — 1200°C, 5 h. A D/MAX-2500 diffractometer (RIGAKU Company) was used to study the samples. It was established that the heat-treatment time had no effect on the phase composition of the samples. The following phases were determined: quartz $SiO_2$, two modifications of $Al_2O_3$ (with orthorhombic and tetragonal lattices), and spinels of the type $MgAl_2O_4$ and $3CaO \cdot 2SiO_2$. The results of the tests and studies were used to choose the optimal composition of the coating $Al_2O_3$ – RO + 5% $ZrO_2$, which was labeled as ÉVT-79.

The use of coatings during heat treatment makes it possible to decrease the oxidizability of VKS steel by a factor of 25 – 30, decrease allowances for mechanical working, and increase the quality of the half-done parts.

The ÉVT-79 PTC is universal because it can be used at different stages of the heat-treatment of VKS steel: tempering, aging, annealing, normalizing, and hardening in a wide range of temperatures — 950 – 1200°C.

The technologies with low energy-intensiveness developed for preparing universal PTC and depositing them on large-size steel parts eliminate the energy-intensive technological operations conventionally used for preparation of PTC — frit making, granulation and grinding, as well as the use of expensive facilities for depositing a coating by the electrostatic method. ÉVT-77M and ÉVT-79 coatings decrease the cost of half-done products by 30%, labor- and energy-intensiveness of the processes by 30 – 50%, and material-intensiveness by 30%, increase the yield of good parts by 10 – 20%, and improve the ecological safety of production.

The fritless glass-ceramic coatings developed for protecting VKS high-strength steel from oxidation and decarbonization will make it possible to obtain the required level of quality and reliability for new high-strength structural steels used in the critical parts of a chassis and the primary parts in civilian aviation.

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